

Bioinspired Structural Color Patterns Derived from 1D Photonic Crystals with High Saturation and Brightness for Double Anti-Counterfeiting Decoration

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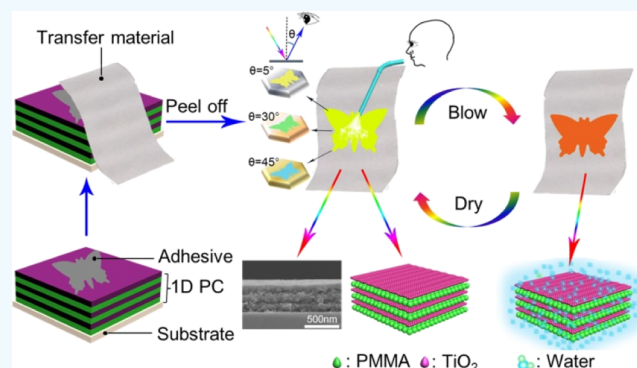
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Supporting Information

ABSTRACT: Imitating the butterfly wing scale with a layer-by-layer structure and angle-dependent property, we present a facile method for the fabrication of flexible, transferable, and multilayered one-dimensional photonic crystal (1D PC) patterns with high color brightness and saturation for anticounterfeiting decoration. The PCs with a thickness less than 1 μm are assembled by alternate spin-coating poly(methyl methacrylate) (PMMA) nanoparticles and titania ones on plane substrates, and their color shade and reflectivity are adjusted by modulating PMMA concentration and stack number, respectively. As the particle-based PMMA layer shows weak binding force with both hydrophilic and hydrophobic substrates, when a certain external force from pressure-sensitive adhesive is exerted on the PC, the thin colorful film can be directly peeled off. With a patterned double-sided adhesive tape, the PCs with various structural color patterns can be transferred and strongly bonded to other flexible or curved substrates. Owing to the dark color of the adhesive, transmitted light is absorbed, and backscattering is effectively lowered to obtain very brilliant structural colors. The transferred PC patterns with beautiful colors show strong angle dependence and environmental stimulus responses because of the sensitive PMMA material and textural pores existing in the PCs. With this method, double anticounterfeiting with higher security and decorative effect is achieved with simple PCs for various product packages.

KEYWORDS: photonic crystals, anti-counterfeiting, structural colors, angle-dependence, stimulus response



1. INTRODUCTION

Photonic crystals (PCs) are periodical nanomaterials that can forbid propagation of certain light wavelengths in them owing to the photonic band gaps.^{1,2} PCs widely exist in nature, for example, in scales of beetles,³ scales and fins of tropical fishes,⁴ *Morpho* rhetenor,⁵ and peacock feathers.⁶ In recent years, study of bionic structural coloration has been intensively concerned because of their functional applications as recognition sensors, photoelectric devices, cell culture, anti-counterfeiting trademark, and so forth.^{7–10} PCs show significant advantages in the anti-counterfeiting area because of their angle-dependence color change, and those with stimulus-responsive properties have been paid much attention so as to strengthen the anti-counterfeiting functions. Imitating the layered structure of the *Morpho didius* butterflies' wings, Meng et al.¹¹ prepared polyvinylidene fluoride structural color films with a double-layer inverse heterostructure for anti-counterfeiting applications. Inspired by *Tmesisternus isabellae*, Bai et al.¹² proposed a kind of colloidal PC pattern with vapor-revealed implicit images by inkjet printing mesoporous colloidal microspheres on rigid and soft substrates, showing prominent potential for anti-counterfeit applications.

Among the structural colors in the natural world, one of the most representative examples is that of butterflies. Multilayer reflectors are the common type of photonic structures existing in butterflies. They may be formed by every component of a scale, such as scutes and flutes, and they are also found within the lumen. In each case, the multilayer reflector consists of alternating layers of chitin (the high refractive index layers) and air (the low refractive index layers).¹³ Inspired by *Morpho* butterfly wings, the researchers successfully prepared tunable structurally colored photocatalysts,¹⁴ novel cellular mechanical visualizable biosensors,¹⁵ artificial structural color pixels, and so forth.¹⁶

In the PC family, one-dimensional PCs (1D PCs), also named Bragg stacks, are composed of two kinds of regular

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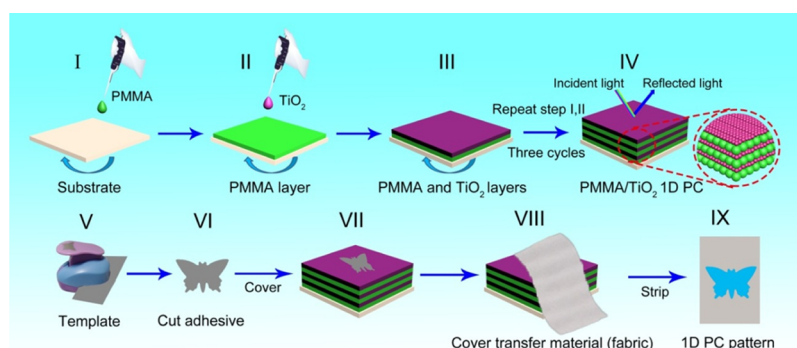


Figure 1. Schematic of fabrication and transfer of flexible PMMA/TiO₂ 1D PCs. (I) Spin-coating PMMA micro-emulsion, (II) spin-coating TiO₂ sol, (III) one stack with a PMMA layer and a TiO₂ layer, (IV) PMMA/TiO₂ 1D PCs with three stacks, (V) butterfly pattern template, (VI) adhesive cut with a template, (VII) covering the butterfly-patterned adhesive on 1D PCs, (VIII) covering the transfer material (fabric), and (IX) transferred 1D PC butterfly pattern on the transfer material.

alternating materials with different refractive indexes along one direction and are similar to the multilayered structure of butterfly wings. They have aroused wide concern because of their simple structure, convenient assembly process, and good application properties.¹ Nevertheless, most traditional 1D PCs assembled on plate silicon wafers or glass substrates by the spin-coating or dipping method^{17–21} were limited to the substrates, so their application range is pretty narrow. At present, the preparation of flexible self-supporting 1D PCs is mainly based on self-assembly of block copolymers and surfactants^{29–32} or by means of sacrificial layers^{33–35} and filling of flexible polymers.^{36–40} In addition, the application of flexible self-supporting PCs in the field of anti-counterfeiting is mainly based on 3D PCs, utilizing angle-dependence^{41–44} or various types of external stimulus responses^{45–48} to achieve anti-counterfeiting. However, there are very few reports on anti-counterfeiting applications of 1D PCs.

Inspired by butterfly wings with scales consisting of multilayers, we designed to prepare transferrable, flexible, and patterned 1D PC films with high color brightness and saturation for anti-counterfeiting decoration. The fabrication and transferring process of a multilayered PC with structural color onto a transfer material (taking a fabric as an example) is presented in Figure 1. First, a kind of nanopolymer—poly(methyl methacrylate) (PMMA) with a low refractive index is spin-coated on a plate substrate to assemble the first layer; after drying, a layer of nano-TiO₂ with a high refractive index is spin-coated on the assembled PMMA nanolayer. They are together called a stack. Several stacks together construct a multilayered 1D PC. On this basis, a cut double-sided adhesive tape with a butterfly pattern and a piece of fabric are in sequence covered on the PC. Through pressing for a while, the structural color film can be directly peeled off and transferred onto the fabric.

In this study, PMMA was selected and spin-coated as the first layer because of its hydrophobicity and poor adhesion to the substrate, facilitating peeling and transferring, and it was prepared as nanoparticles, which can reduce the contact area with the substrate and further decrease bonding force. In addition, the all-nanoparticle assembly is beneficial for obtaining clear interlayer boundaries and realizing external stimulus response because of the existence of nanopores within the particles. The theoretical refractive indexes of anatase TiO₂ and PMMA were 2.4 and 1.49, respectively. The big contrast was conducive to the 1D PC films to obtain bright color.¹⁹ In

the study, a solid polyacrylate adhesive tape was chosen as a transfer medium because of its high adhesion strength, environmental friendliness, and wide material suitability.⁴⁹ Furthermore, it can be applied in food packaging and medical equipment. Herein, a polyacrylate pressure-sensitive adhesive tape was used for pattern transferring which could overcome the problems that the liquid adhesive was easy to flow and difficult to control the clear pattern boundary. Meanwhile, dark color adhesive was designed to use for that transmitted light could be absorbed and backscattering was effectively lowered to enhance the contrast of the color. Because of this special design, the obtained flexible PC patterns display angle-dependent brilliant color and vapochromic and solvatochromic properties. This is the first time to use this PC structure and transferring method to obtain flexible brilliant colors with double anti-counterfeiting and decoration functions.

2. EXPERIMENTAL SECTION

2.1. Materials. Anatase nano-TiO₂ and methyl methacrylate (MMA, 99.5%) were purchased from Xuancheng Jingrui New Materials Company and Tianjin Bodi Chemical Co., Ltd., respectively. Sodium dodecyl sulfate (SDS), potassium persulfate (KPS), and ethanol were supplied by local suppliers. Polyvinyl chloride, polycarbonate, and polypropylene plate substrates, which were colorless, transparent, and smooth, were purchased from Lian-jia Plastic Products Co., Ltd. The glass and other chemicals were obtained from local suppliers. The double-side pressure-sensitive adhesive tape was purchased from Shenzhen Chang-da Sheng Electronics Co., Ltd. Pattern templates were purchased from Yiwu Qing-chun Stationery Co., Ltd.

2.2. Preparation of PMMA Nanoparticles and TiO₂ Sol. Polymer nanoparticles were prepared via a modified micro-emulsion polymerization.^{19,20} To begin with, pre-emulsion was synthesized with 30.0 g of H₂O, 1.25 g of SDS, and 2.0 g of MMA in a 250 mL flask and heated to 75 °C. Then, 0.075 g of KPS was fully dissolved in 3 mL of water. Two milliliters of the abovementioned KPS solution was added to the flask. Then, the polymerization was implemented under stirring for 10 min. Then, the remaining KPS solution was added, and the remaining 18 g of the MMA monomer was slowly added to the flask and reacted for 1 h. The weight-average molecular weight (*M_w*) of PMMA was measured to be 244,784 g/mol and its polydispersity index (PDI) was 1.376. TiO₂ colloid was obtained by dispersing anatase TiO₂ powder into a mixed solvent of ethanol/water with a 1:1 mass ratio.

2.3. Assembly of 1D PCs. First, polycarbonate substrates were washed with ethanol three times. After being blow-dried, hydrophilic treatment was carried out in an oxygen plasma cleaner (Shenyang Kejing PCE-6) for 180 s. 1D PC films were fabricated on the

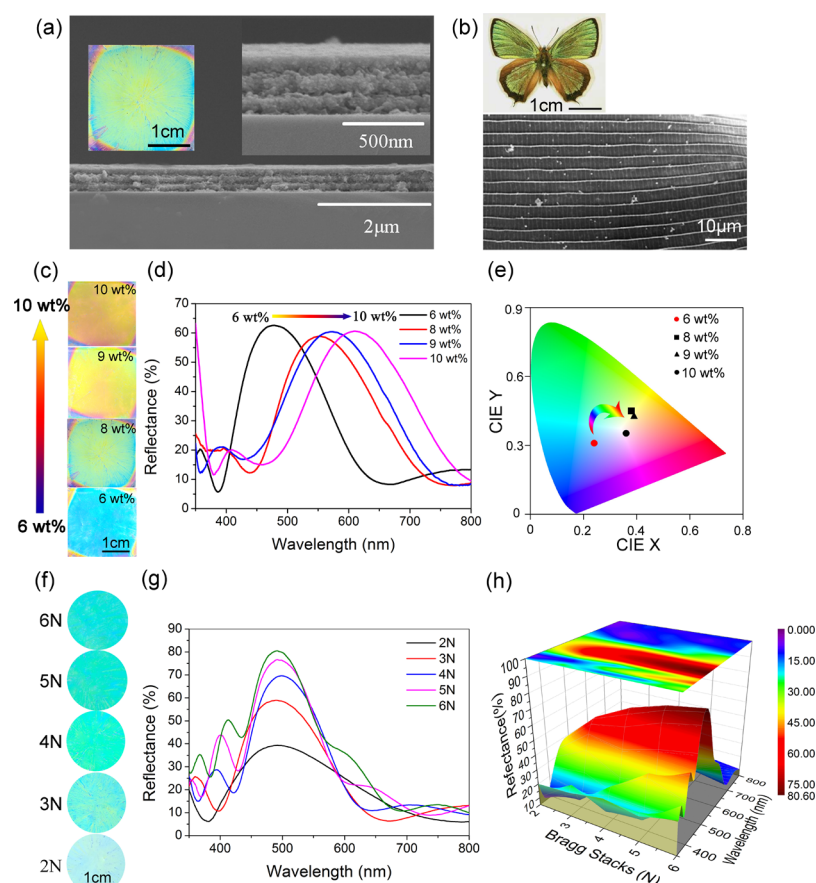


Figure 2. (a) Digital photo and SEM image of PMMA/TiO₂ 1D PCs with three stacks; (b) digital photo and SEM image of a scale of *C. brillantinus*;⁵³ (c) digital photos, (d) reflectance spectra, and (e) CIE 1931 chromaticity coordinates of PMMA/TiO₂ 1D PCs with different PMMA concentrations; and (f) digital photos, (g) reflectance spectra, and (h) 3D color map surface of the 1D PC films with different Bragg stacks (the detecting angle of the spectra and the viewing angle of the samples were both 5°). The digital photo and SEM image shown in Figure 2b were reproduced with permission from ref 53, Copyright [2009] The Royal Society (U.K.).

substrates via alternate spin-coating PMMA micro-emulsion and 3% TiO₂ sol (Laurell WS-650SZ-6NPP/LITE). The spin time and rate were 40 s and 5000 rpm, respectively. The bottom layer was PMMA and the top layer was titania in all the experiments. PMMA and TiO₂ layers were heated at 60 °C for 1 min and then treated in an oxygen plasma cleaner for 120 s after each spin-coating step. The method and parameters for constructing 1D PCs on other substrates are the same as mentioned above.

2.4. Transfer of 1D PCs. The polyacrylate double-sided pressure-sensitive adhesive tape was cut into various patterns with templates and one side was pasted on the surface of the assembled PC film. Next, other substrate materials, including metal, paper, plastic, and textile, were covered on the other side of the patterned tape and moderate pressure was applied. The transfer of 1D PCs on the fabric was realized by direct stripping. The 180° peel strength of the tape was measured using an electronic stripping tester (BLD-2005, Labthink, China).

2.5. Water Vapor and Solvent Response. The water vapor response of a flexible 1D PC pattern is tested by a human blowing through a straw. Similarly, the solvent response is achieved by two ways, one by dropping water on the 1D PC patterns and the other by soaking the pattern into the solvent (water or ethanol). The reflectance spectra of the 1D PC films were obtained using a fiber optic spectrometer (EQ2000, Choptics, China).

2.6. Characterization of 1D PCs. The images of 1D PCs were obtained using a digital camera (D7000, Nikon, Japan). Reflectance spectra were measured using a spectrophotometer (U-4100, Hitachi, Japan). Except other stated, the incident angles were all 5°. The refractive indexes were determined using an Ellip-ER-III spectroscopic

ellipsometer. Gel permeation chromatography (TDA 302 Triple Detector Array, Viscotek, USA) was carried out to determine the molecular weight and molecular weight distribution of the polymer. The particle size and zeta potential of PMMA and TiO₂ were measured by dynamic light scattering spectroscopy (Zetasizer nano series Nano-ZS100, Malvern, UK). The Fourier transform infrared spectra of the dried PMMA were characterized using a spectrometer (6700, ThermoFisher, USA). Scanning electron microscopy (SEM) images of 1D PCs were obtained using an ultrahigh resolution scanning electron microscope (SU8220, Hitachi, Japan). Thermal properties of the dried PMMA were measured using a differential scanning calorimeter (Q2000, TA Instruments, USA).

3. RESULTS AND DISCUSSION

3.1. Preparation and Characterization of the 1D PCs with Structural Colors. Bragg's law in eq S1^{50,51} shows that to obtain 1D PCs with structural colors, each layer thickness should be strictly controlled. The better particle size for assembly is usually at 5–50 nm for obtaining smooth interfaces and good optical properties.⁵² Figure S1a,c presents that the prepared PMMA particles have an average diameter of 35.06 nm and a PDI of 0.16; and the diameter of TiO₂ is 26.80 nm and its PDI is 0.19. Their SEM images shown in Figure S1b,d demonstrate that both PMMA and TiO₂ are very small particles with the size less than 50 nm. Zeta potential results present that the surface charges of PMMA and TiO₂ particles are −46.30 and +39.70 mV, respectively. In addition, the

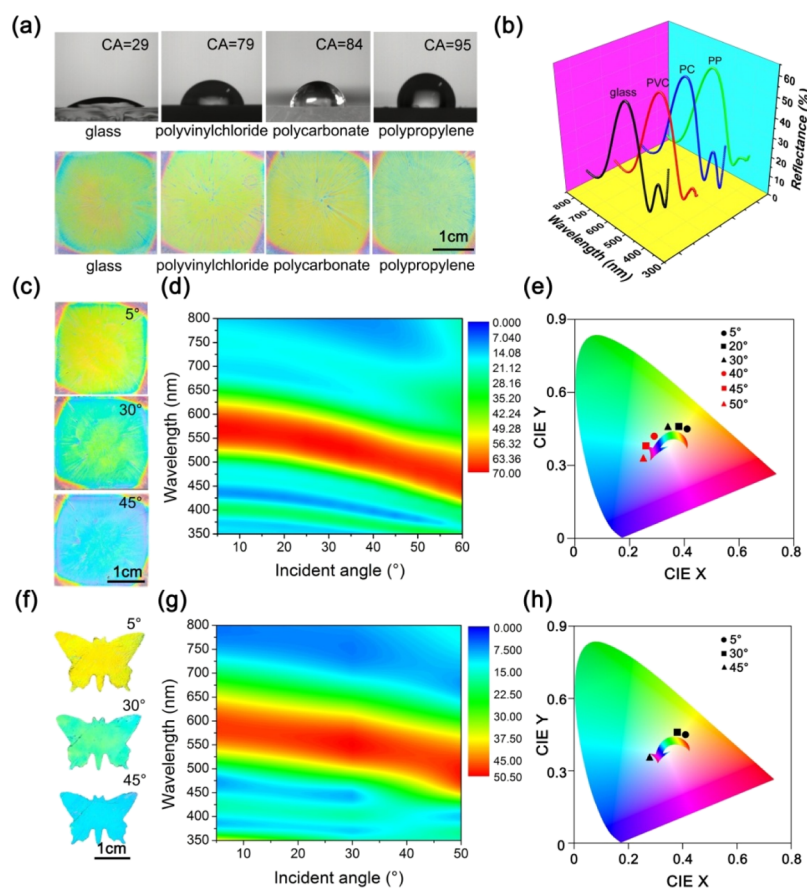


Figure 3. (a) Water contact angles of different substrates, digital photos, and (b) reflectance spectra of PMMA/TiO₂ 1D PCs fabricated on substrates with different water contact angles; (c) digital photos, (d) reflectance spectra, and (e) CIE 1931 chromaticity coordinates of PMMA/TiO₂ 1D PCs fabricated on polycarbonate substrates with different incident angles; and (f) digital photos, (g) reflectance spectra, and (h) CIE 1931 chromaticity coordinates of flexible 1D PC patterns with different incident angles.

positive TiO₂ and negative polymer facilitated layer-by-layer assembly, and the electrostatic attraction made the layers of the 1D PC film firmly bonded. Attenuated total reflectance–IR result in Figure S2 shows that no C=C characteristic absorption peak (1600–1680 cm⁻¹) exists, which verifies that monomer MMA has been completely polymerized. The absorption peak at 1731.37 cm⁻¹ is attributed to the stretching vibration of C=O of ester of PMMA, and the peaks at 1149.82 and 1193.49 cm⁻¹ are assigned to the stretching vibration of C–O–C of the ester. Figure S3 displays that *T_g* and thermal decomposition temperature of PMMA are 128.63 and 373.70 °C, respectively, indicating that it has good thermal stability.

Figure 2a shows a yellow-green 1D PC sample fabricated with 8 wt % PMMA and 3 wt % TiO₂ on the polycarbonate substrate. Before assembly, hydrophilic treatment of the substrate was carried out, and the water contact angle changed from 84 to 49.5°, which benefited diffusion and spin-coating of water-based PMMA micro-emulsion on the substrate. The assembled PC film had a distinct layer-by-layer structure, as shown in field emission SEM image of Figure 2a, which was similar to the multilayer structure of the lycaenid butterfly (*Chrysozephyrus brillantinus*) wing scale⁵³ (Figure 2b). In addition, the average thicknesses of the PMMA and TiO₂ layers after multipoint measurement and calculation were 55 and 112 nm, respectively. These approximately corresponded to about two PMMA nanoparticle and four TiO₂ nanoparticle diameters, respectively. The refractive index of PMMA and

TiO₂ measured using a spectroscopic ellipsometer was 1.395 and 1.780, respectively. According to the refractive index data and the layer thickness, the maximum reflection wavelength is calculated to be 552.17 nm based on Bragg's law eq S2,⁵⁴ which is consistent with the wavelength of the digital photo color.

By changing the mass fraction of PMMA colloidal nanoparticles for assembly, the layer thickness was adjusted. Then, 1D PCs with different colors can be prepared based on Bragg's law.^{50,51} According to the law, when the thickness of PCs increases, the photonic band gap red-shifts and the color changes toward the long-wavelength direction. Figure 2c shows that when PMMA concentration increases from 6 to 8, 9, and 10 wt %, the color changes from blue to yellow-green, yellow, and orange, respectively. Figure 2d shows the corresponding reflection spectra and it presents that the maximum reflection wavelength varies from 477 to 554, 577, and 610 nm, respectively, which is consistent with the colors of the digital photographs. Figure 2e depicts the CIE 1931 chromaticity coordinate of the 1D PC by varying the mass fraction of PMMA. With the increase in the concentration of PMMA, the color coordinate turns from blue to yellow-green, then to yellow, and finally to orange.

Reflectivity of 1D PCs can be explained using eq S3.²⁰ It can be seen from this formula that by increasing the number of Bragg stacks, the reflectivity will be enhanced; thus, the color strength of the PC film will be increased. As shown in Figure 2f, the color strength of the digital photos was gradually

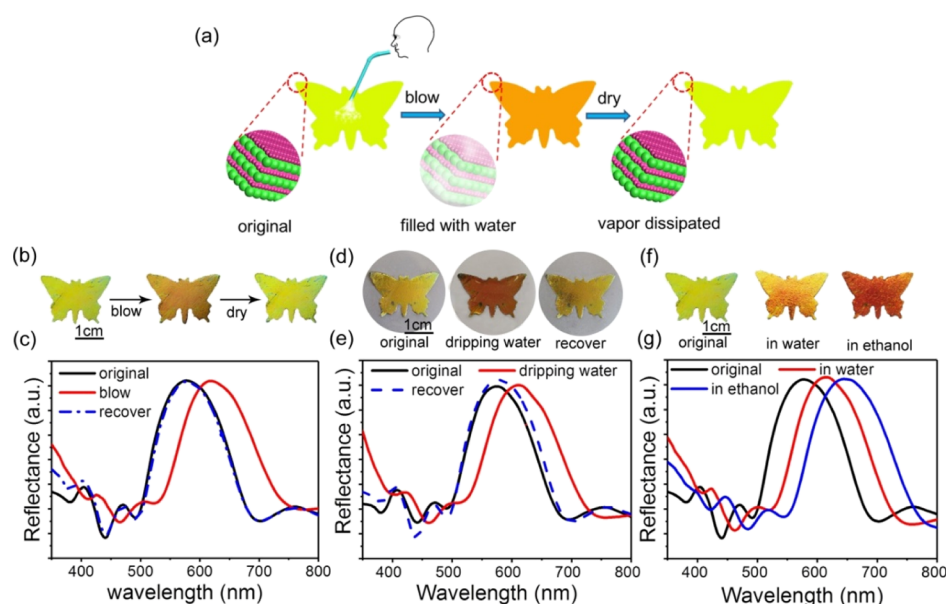


Figure 4. (a) Schematic diagram, (b) digital photos of color change, and (c) reflectance spectra of flexible 1D PC butterfly patterns in the process of blowing and drying; (d) digital photos of color change and (e) reflectance spectra of flexible 1D PC butterfly patterns in the process of water-dripping and drying; and (f) digital photos and (g) reflectance spectra of 1D PC butterfly patterns dip in different solvents (the detecting angle of the spectra and the viewing angle of the samples were both 5°).

enhanced as the number of Bragg stacks increased from 2 to 6, and the reflectivity at the maximum reflection peak increased from 39.0 to 81.0%, respectively, as presented in Figure 2g. The reflectance spectra in the form of 3D color map surface (Figure 2h) vividly revealed that the reflectivity enhanced as the Bragg stack increased, and the position of the maximum reflection peak kept at around 490 nm.

3.2. 1D PCs Assembled on Different Substrates and the Angle-Dependence Property before and after Transferring. In this study, the flexible 1D PCs can not only realize the adjustment of colors, their brightness, and saturation but also realize assembly and transferring from substrates with different hydrophilic and hydrophobic properties. Figure 3a depicts that water contact angles of glass, polyvinyl chloride, polycarbonate, and polypropylene substrates are 29, 79, 84, and 95° , respectively. The hydrophobic substrates need to be pretreated with oxygen plasma before PC assembly, and then, the surfaces would temporarily show hydrophilicity to benefit spin-coating of PMMA dispersing in water. Using 8 wt % PMMA and 3 wt % TiO_2 , bright yellow-green colors can be fabricated on all the substrates mentioned above. Owing to different refractive indexes of the substrates, the PC colors showed certain differences with the positions of the reflection peak all near 540 nm (see Figure 3b). After drying, the PCs can be directly peeled off from all the substrates with the aid of the polyacrylate pressure-sensitive tape. The transmission and absorption spectra shown in Figure S4 indicated that the light transmittance was between 2 and 2.5% and the absorbance was greater than 1.25, so transmitted light could be effectively absorbed to enhance the contrast of the color. The maximum tensile stress of the adhesive shown in Figure S5 was 2.15 MPa, and the compressive stress was 0.54 MPa, indicating its good mechanical properties. Table S1 shows the 180° peel strength of PC by the double-sided pressure-sensitive tape from glass, polyvinyl chloride, polycarbonate, and polypropylene was measured to be 0.60, 0.31, 0.28, and 0.25 N/mm, respectively. The data presented that

with the increase in the hydrophobicity, the peel strength decreased, indicating that the lower surface energy will facilitate the peeling process. It was also measured that the 180° peel strength of the double-sized and single-sized polyacrylate pressure-sensitive tape and commonly used Scotch tape was 1.09, 0.58, and 0.26 N/mm, respectively. With the polyacrylate tape, especially the double-sized one, its peel strength is much larger than that for peeling off the PC from the substrates; therefore, the structurally colored films can be easily transferred using the double-sized polyacrylate tape.

Figure 3c–h shows both the prepared 1D PCs and the transferred ones having strong angle dependence, which conforms to Bragg's law. When the incident angle of light increases, the photonic band gap blue-shifts and the color of the 1D PC film shifts toward the short-wavelength direction. Figure 3c shows digital photos at different incident light angles. When the incident angle increased from 5° to 30° and 45° , the 1D PC film changed from yellow to green and blue, respectively. The reflectance spectra shown in Figure 3d reveal the blue-shift trend of the position of the reflection peak as the incident light angle increases. As the angle gradually increases from 5° to 60° , the photonic band gap position varied from 577 to 453.5 nm, respectively, and the maximum displacement reaches 114.5 nm. Figure 3e depicts the CIE 1931 chromaticity coordinate of the 1D PC at various incident angles. With the increase in the angle, the color coordinate moves from yellow to green and then to blue gradually.

Meanwhile, the 1D PC butterfly patterns after transferring also have the characteristic of angle dependence. As the incident light angle increases from 5° to 30° and then to 45° , the color of the PC butterfly pattern varied from yellow to green and then to blue, respectively (Figure 3f and Video S1). Likewise, the reflectance spectra (Figure 3g) clearly demonstrated that the maximum reflection wavelength shifted from 577 to 492 nm. In addition, the CIE 1931 chromaticity coordinate of the butterfly patterns at various incident angles

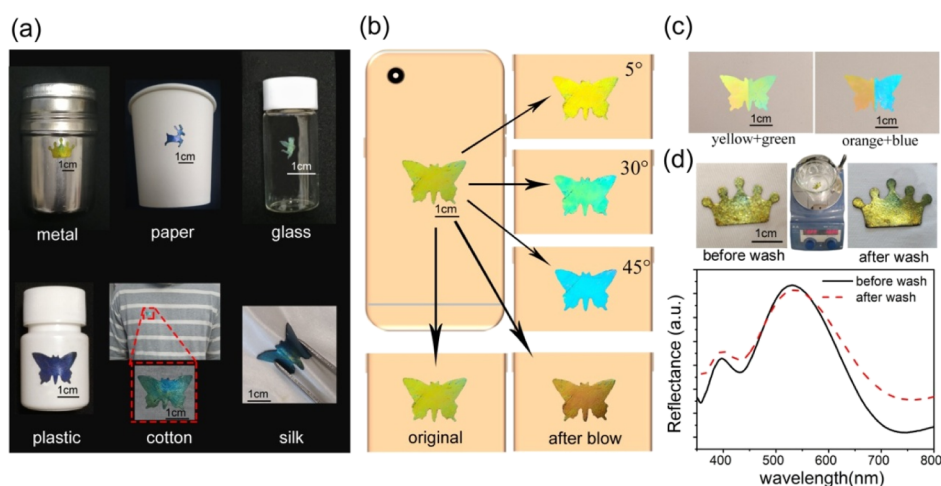


Figure 5. (a) Digital photographs displaying various flexible PMMA/TiO₂ 1D PC patterns transferred onto metal, paper cup, glass, plastic medicine bottle, cotton fabrics, and silk, respectively; (b) angle-dependence and water vapor response of 1D PC butterfly patterns transferred onto a smart phone; (c) double-color 1D PC butterfly patterns after transferring; and (d) water washing test of flexible 1D PC patterns after transfer printing.

showed that the position indicating the color gradually moved from yellow to green and then to blue (Figure 3h). In the view of the abovementioned characteristics of strong angle dependence, the transferred 1D PC patterns have a high application value in the field of anti-counterfeiting.

3.3. Water and Ethanol Response. In addition to high angle dependence, the flexible 1D PC patterns also have good water vapor response, which can be easily achieved by human blowing; as the response process is simple and convenient to realize, it shows much advantage in the field of anti-counterfeiting.

Figure 4a shows a schematic diagram of flexible 1D PC butterfly patterns in the process of blowing and drying. When people blew through a straw on the PC surface, the water vapor which quickly diffused into the microchannel of the 1D PC caused an increase in refractive indexes of PMMA and TiO₂ layers, which made the photonic band gap of the PC pattern red-shifted, and the structural color changed toward the direction of the long wavelength. As the water vapor dissipated, the refractive index of 1D PCs changed back, and the position of the photonic band gap and the PC color recovered. It is measured using an Ellip-ER-III spectroscopic ellipsometer, the refractive index of PMMA increased from 1.395 to 1.420, and the refractive index of TiO₂ increased from 1.780 to 1.830 because of infiltration of water vapor inside the pores under the condition of human blow. Figure 4b and Video S2 display the color variation of the 1D PC butterfly patterns during the blowing and recovering process, which demonstrated that the color changed from yellow-green to orange quickly after blowing and returned to yellow-green when blowing was stopped. The reflectance spectra in Figure 4c show that the maximum reflected wavelength moved from 577 to 619 nm after blowing and then returned to 577 nm, corresponding to the colors of the digital photos, as shown in Figure 4b.

In addition, the structural color of the flexible 1D PC pattern can also be changed through response to water or ethanol. Both water and ethanol are common, cheap, and nontoxic solvents, making them convenient to use for anti-counterfeiting testing. Figure 4d displays the digital photographs of color change in flexible 1D PC butterfly patterns in the process of water-dripping and drying. As the water dropped onto the 1D

PC, the water molecules diffused into its internal pores, causing an increase in the refractive index. Then, the photonic band gap red-shifted and the color changed from the original yellow-green to orange. After drying, the flexible pattern can return to its original yellow-green color. This phenomenon is further supported by the reflection spectra, as shown in Figure 4e, which presents that the reflection peak increased from 577 to 612 nm after water dripping and recovered to 577 nm after drying. Figure 4f reveals the color change in the flexible 1D PC pattern after it was immersed in the water and ethanol solvent, respectively. Because the refractive index of ethanol (1.36) is greater than that of water (1.33) and ethanol can cause PMMA to swell, the film thickness and the refractive index of 1D PCs changed more and the photonic band gap produced a greater red shift. It can be seen that when the flexible butterfly pattern was immersed in water, the color changed from yellow-green to orange, while to red when immersed in ethanol. The reflectance spectra (in Figure 4g) showed that the reflection peak shifted from 577 to 614 and 647 nm, respectively, when being immersed in water and ethanol, respectively, which was in good accordance with the structural color change (in Figure 4f). Figure S6 demonstrates that the 1D PCs have good reversibility after 10 cycle responsive tests in the process of blowing and water-dripping.

3.4. Patterns of the Flexible 1D PC Films and Their Anti-Counterfeiting Effect. In the view of the abovementioned angle dependence and external stimulus response, the 1D PC patterns are designed to be transferred to various packaging materials for anti-counterfeiting decoration. Digital photographs (Figure 5a) showed that various flexible PC patterns were transferred to a metal bottle, paper cup, glass bottle, plastic medicine bottle, cotton fabrics, and silk. Taking a mobile phone as an example, Figure 5b reveals the anti-counterfeiting effect of the 1D PC structural color pattern utilizing its angle-dependence and water vapor response. When the light incident angle increased from 5 to 30 and 45°, the structural color of the butterfly pattern varied from yellow to green and blue, respectively. When a person blew on the pattern, the color of the butterfly quickly varied from yellow-green to orange. The double-color 1D PC butterfly patterns shown in Figure 5c were also achieved by transferring from different PC structural colors, which enhanced diversity of

coloration and realized double-color anti-counterfeiting. The water washing test on the transferred structural color pattern on textile was performed at a stirring speed of 1000 r/min for 1 h (Figure 5d). The color of the 1D PC pattern before and after washing almost did not change, and the maximum reflection wavelength remained at 532 nm, indicating good mechanical stability and bonding strength. Figure S7 shows that the maximum reflection wavelength of the 1D PC film was maintained at 550 nm when the temperature gradually increased from 30 to 80 °C, indicating its good temperature stability.

Based on the abovementioned analysis, on the one hand, the 1D PC patterns after being transferred have clear boundary and bright, adjustable, and stable structural colors, which can play a decorative role; on the other hand, double anti-counterfeiting can be achieved by angle-dependent and water vapor or solvent-based color change. For instance, when being used on a drug bottle, the PC patterns can prevent the spread of fake medicine owing to double anti-counterfeiting characteristics and at the same time, make the patient in good mood for the beautiful structural colors.

4. CONCLUSIONS

In brief, inspired by butterfly wings with scales consisting of multilayers, the pattern transferring of flexible 1D PC films from substrates with different surface energies to a variety of materials was achieved by means of polyacrylate pressure-sensitive adhesives. The transferred PC patterns have strong angle dependence and sensitive water vapor and solvent response. Thanks to solid pressure-sensitive adhesive tapes, the transferred structural color patterns have clear and complete boundaries and high bonding strength. Meantime, the dark color adhesive could absorb transmitted light, and back-scattering was effectively lowered to enhance the contrast of the color. Based on the abovementioned characteristics, the flexible 1D PC patterns after transferring have promising application prospect in achieving double anti-counterfeiting and decorative effects on various types of package (such as medicine, skin care products, etc.). This biomimetic structural color film can not only realize the environmentally friendly patterned decoration of various packages but also greatly improve the anti-counterfeiting effect.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsapm.0c00047>.

Equations of Bragg's law, particle size distribution and SEM image of PMMA nanoparticles and TiO₂ nanoparticles, Fourier-transform infrared spectrum of dried solid PMMA nanoparticles, differential scanning calorimetry curve of PMMA, thermogravimetric analysis thermogram of PMMA, 180° peel strength of PMMA/TiO₂ 1D PCs from different substrates, 180° peel strength of different adhesives from steel plate, transmission and absorption spectra of the double-side polyacrylate pressure-sensitive adhesive tape, compression and tensile performance test of the double-side polyacrylate pressure-sensitive adhesive tape, cycle responsive tests of PMMA/TiO₂ 1D PCs, and contour plot of reflectance spectra of PMMA/TiO₂ 1D PCs at different temperatures (PDF)

Color change in the PC butterfly pattern from yellow to green and then to blue (MP4)

Color variation of the 1D PC butterfly pattern during the blowing and recovering process (MP4)

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Notes

The authors declare no competing financial interest.

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